Matrix-Isolation Study of the Low-Pressure Pyrolysis and Ultraviolet Photolysis of Dimethyl Peroxides and of CF_3OCl

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Abstract: The low-pressure pyrolysis and uv photolysis of CH_3OOCH_3, CD_3OOCD_3, CF_3OOCF_3, and CF_3OCl were studied to obtain information on the initial decomposition steps. The decomposition products were trapped at 8°K in an argon matrix and identified by infrared spectroscopy. The main products in the pyrolysis and photolysis of CH_3OOCH_3 or CD_3OOCD_3 are formaldehyde and methanol. The pyrolysis of CF_3OOCF_3 yielded COF_2 and CO_2 as main products. In addition, a novel unstable species was produced having its strongest infrared absorptions at 1592 and 1025 cm^{-1}. The decomposition of CF_3OCl resulted in COF_2 as the only detectable product.

The thermal decomposition[1] and uv photolysis[2,3] of dimethyl peroxide (DMP) have previously been investigated. The decomposition products were identified by gas-phase infrared spectroscopy,[1] a combination of manometric and chemical analysis,[2] and gas-chromatographic analysis.[3] The split of the O–O bond was postulated as the initial, rate-determining step for both the thermal[1] and photolytic[3] decomposition, as expected from bond-energy considerations (D(O–O) = 36.1, D(H–C) $\sim$ 92, D(C–O) $\sim$ 91 kcal).[4] However, the previously used experimental techniques[1-3] did not allow a study of the exact nature of the products of the initial decomposition steps. A low-pressure decomposition of DMP (diluted by Ar) followed by immediate trapping of the products in an Ar matrix at 8°K might allow the isolation of highly reactive, short-lived intermediates and thus allow conclusions about the initial decomposition steps. The conspicuous lack of information on isolated methoxyl radicals[5] in the literature adds further interest to the problem.

Experimental Section

Reagents. The DMP was prepared by the method of Hanst and Calvert.[1] It was purified in a Pyrex-glass vacuum system by fractional condensation through a series of traps kept at −78, −95, and −111°. The trap kept at −111° contained most of the DMP. The only impurity detectable by infrared spectroscopy was a small amount of methyl formate which could not be separated from DMP by means of fractional condensation. Treatment of the DMP with aqueous KOH and H_2O_2, followed by fractional condensation, reduced the percentage of CH_3OCHO but also destroyed some of the DMP. In order to obtain DMP free of CH_3OCHO the method of Hanst and Calvert[1] was slightly modified by using a small excess of KOH. The DMP thus prepared and purified by fractional condensation showed no detectable impurities in the infrared and Raman spectra. The perdeuterated DMP was prepared and purified in a similar manner, using $CD_3OSO_2OCD_3$, however, instead of $CH_3OSO_2OCH_3$.

Caution! Liquid DMP is shock sensitive[6] and should be handled only with proper shielding.

Perdeuterated dimethyl sulfate was prepared by the method[7] of Morse, *et al.*, from CD_3OD and chlorosulfonic acid. However, it was found advantageous to use twice as much CD_3OD as recommended[7] by Morse, *et al.* Gas-chromatographic analysis of the distilled $CD_3OSO_2OCD_3$ showed no detectable impurity.

The CF_3OCl was prepared and purified by the method[8] of Schack and Maya. It was handled exclusively in a prepassivated stainless-steel–Teflon FEP vacuum system.

The CF_3OOCF_3 was prepared from CF_3OCl by the method[8] of Schack and Maya. It was purified by fractional condensation through a series of traps kept at −126, −142, and −196°. The −142° trap contained the CF_3OOCF_3 and Cl_2. The Cl_2 was removed by washing with dilute aqueous NaOH. The material was refractionated through two traps kept at −126 and −142°. The infrared spectrum of the contents of the −142° trap showed only bands due to CF_3OOCF_3.

The CD_3OD was purchased from Diaprep Inc. and was used without further purification. The only impurity detectable by infrared was CD_3OH. The CH_3OH (spectrophotometric grade from J. T. Baker Chemical Co.) and argon (research grade, 99.9995% minimum from the Matheson Co.) were used without further purification.

Apparatus. The infrared spectra were recorded with a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard gas calibration points.[9] A Cryo-Tip Model AC-3L cryostat (Air Products Corp.) equipped with a Model WMX-1 vacuum shroud was used for the low-temperature studies. The cryostat was operated with compressed H_2 and He in the temperature range 6.5–50°K. Cesium iodide windows were used for the infrared measurements and Suprasil II windows (Amersil Inc.) were used for the photolysis. Temperatures were measured with a Au–Fe *vs.* Cu thermocouple imbedded in indium in a hole drilled into the CsI window. The gas mixtures were prepared by standard manometric techniques in a stainless-steel–Teflon FEP vacuum system connected directly to the sample inlet system. The sample inlet system consisted of a micrometer valve (Whitney, 22 series) and a thin-walled nickel tube ($^1/_{16}$-in. o.d., 60 cm long, wound to a coil). The nickel tube was on the low-pressure side of the micrometer valve and could be heated up to 400°. The pressure inside the shroud was kept at 1-2 $\times$ 10^{-6} Torr. The gas mixtures were deposited at rates between 20 and 200 μmol/min and the deposit rates were manometrically monitored by feeding from a known volume. For the photolysis experiments a Hanovia Model 30620 mercury arc (100 W) with a water filter (transmission 2200–9000 Å) was used. The samples were photolyzed either during or after deposition. For controlled diffusion experiments the He flow to the refrigerator was cut off temporarily until the internal window reached a temperature of about 40–41°K.

Results

Pyrolysis of DMP. Figure 1 shows the results obtained for the thermal decomposition of dimethyl peroxide. In all experiments the Ar-to-DMP mole ratio of the starting material was 400 and the temperature

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(1) P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 104 (1959).

(2) Y. Takezaki, T. Miyazaki, and N. Nakahara, *J. Chem. Phys.*, **25**, 536 (1956).

(3) L. M. Toth and H. S. Johnston, *J. Amer. Chem. Soc.*, **91**, 1276 (1969).

(4) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(5) B. Mile, *Angew. Chem., Int. Ed. Engl.*, **7**, 507 (1968).

(6) G. Baker, R. Pape, and R. Shaw, *Chem. Ind.* (*London*), **48**, 1988 (1964).

(7) A. T. Morse, T. F. Massiah, and L. C. Leitch, *Can. J. Chem.*, **37**, 1 (1959).

(8) C. J. Schack and W. Maya, *J. Amer. Chem. Soc.*, **91**, 2902 (1969).

(9) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Nat. Bur. Stand., Sect. A*, **64**, 841 (1960).

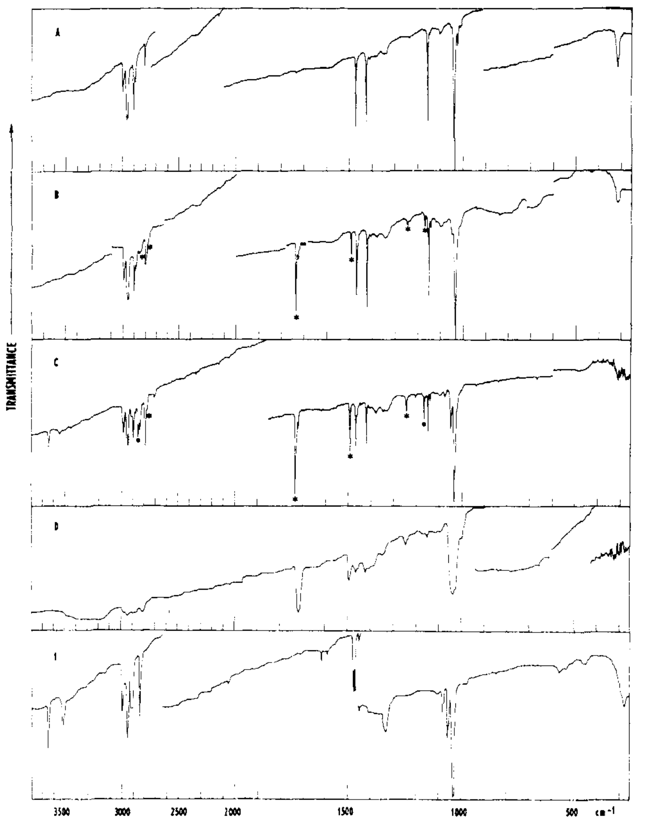

Figure 1. Pyrolysis of CH_3OOCH_3. For explanatory remarks, see Results section.

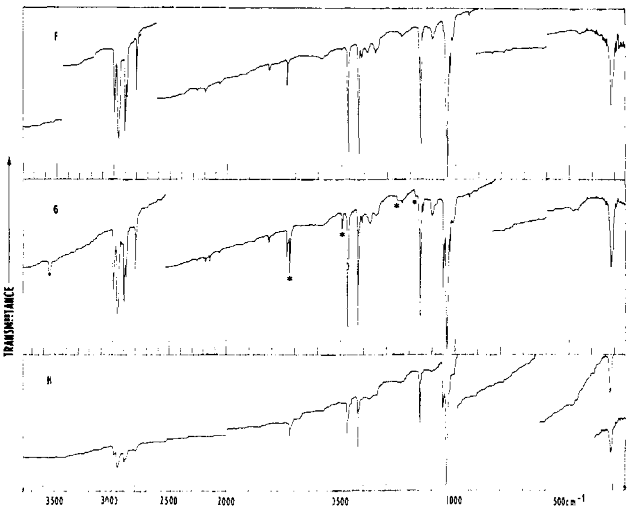

Figure 2. Photolysis of CH_3OOCH_3. For explanatory remarks, see Results section.

of the internal cell window was kept between 8.5 and 10.5°K. Trace A shows the infrared spectrum of neat DMP in Ar deposited at an inlet tube temperature of 25°. Trace B shows the spectrum obtained by heating the inlet tube to 190° during sample deposition. As can be seen, most of the bands are due to undecomposed DMP. In addition to the bands due to DMP, new absorptions have appeared. The bands marked by an asterisk are due to formaldehyde. Their frequencies agree well with those reported for gaseous CH_2O[10] and CH_2O in CO[11] and Ar + Ne[12] matrices. In addition, some CH_3OH (bands at 1050 and 1464 cm^{-1}) has formed. Increasing the inlet temperature to 205° (trace C) results in the formation of more CH_2O at the expense of the DMP. In addition to CH_2O and DMP trace C also exhibits bands due to CH_3OH. Since the matrix spectrum of CH_3OH was reported only for the range of the OH stretching vibrations,[13] we have recorded the spectrum of CH_3OH in argon matrix (mole ratio = 400) as shown by trace E. The appearance of at least two distinct O-H stretching vibrations can be attributed[13] to monomeric and dimeric CH_3OH. The ratio of monomeric to polymeric CH_3OH is a function of the mole ratio[13] and, hence, is higher for trace C than for trace E. It appears that no appreciable amounts of a new unknown species have formed, since all spectral bands (except for the absorption at 2800 cm^{-1} being somewhat too intense) can be ascribed to a mixture of DMP, CH_2O, and CH_3OH. This is also confirmed by the results of a controlled-diffusion experiment (trace D). The deposit of trace C was shortly warmed to 42°K and then recooled to 8.5°K. In spite of the considerable band broadening, no dramatic changes have occurred, indicating that the major absorptions must be due to thermally stable species such as DMP, CH_2O, or CH_3OH. No indication for the formation of detectable amounts of CO was obtained in any of the thermal decomposition runs. However, it should be kept in mind that CO is a relatively weak absorber in the infrared region.

Uv Photolysis of DMP. Figure 2 shows the results obtained for the photolytic decomposition of DMP. The mole ratio between Ar and DMP was again 400 and the temperature of the internal window was kept in all experiments at 8.5°K. A water filter was used in all photolytic experiments. Trace F shows a deposit of DMP in argon before uv irradiation. The sample contained a trace amount of CH_2O formed during storage of the starting material. Trace G shows the same deposit after a 40-min exposure at 8.5°K to uv irradiation. As can be seen, several changes have occurred in the spectrum. There are new absorptions in the region of the characteristic CH_3OH absorptions; however, the frequencies of the OH stretching and deformation vibrations are close to those of dimeric CH_3OH. Furthermore, bands due to CH_2O have appeared; however, the frequency of the C=O stretching vibration has decreased by about 15 cm^{-1} compared to that of neat CH_2O in Ar matrix. The absence of bands due to monomeric CH_3OH combined with these frequency shifts suggests the presence of CH_3OH and CH_2O in the same matrix cage with the frequency shifts observed for the OH and C=O vibrations being due to hydrogen bonding. The frequencies are shifted in the expected directions, *i.e.*, ν_{OH} and $\nu_{C=O}$ have decreased, whereas δ_{OH} has increased when compared with the unassociated molecules. Trace H shows the spectrum obtained when the Ar–DMP mixture was irradiated during sample deposition. The spectrum is in general appearance similar to that of trace G, but its quality is not quite as good. It shows again CH_2O and a barely detectable amount of CH_3OH being in the same matrix cage. The

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(10) H. H. Blau and H. H. Nielsen, *J. Mol. Spectrosc.*, 1, 124, (1957).

(11) G. E. Ewing, W. E. Thompson, and G. C. Pimentel, *J. Chem. Phys.*, 32, 927 (1960).

(12) J. F. Ogilvie, *Spectrochim. Acta, Part A*, 23, 737 (1967).

(13) M. Van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.*, 27, 95 (1957).

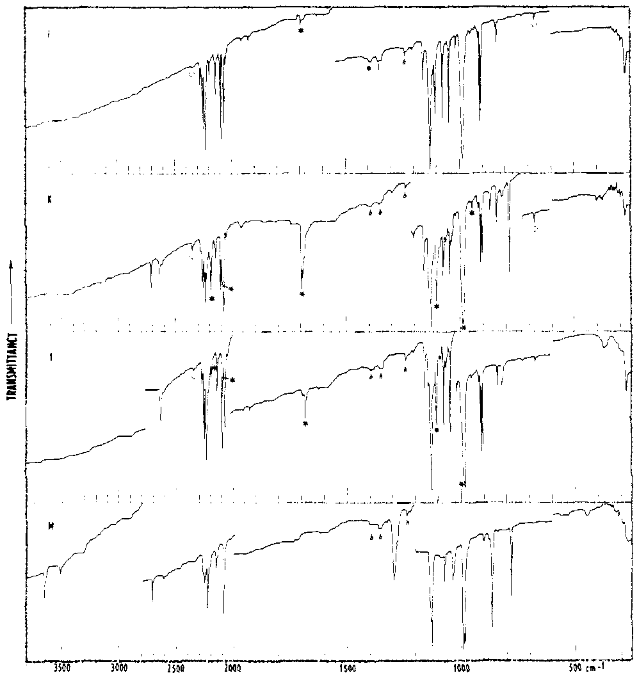

Figure 3. Pyrolysis and photolysis of CD_3OOCD_3. For explanatory remarks, see Results section.

absence of bands due to unassociated CH_2O indicates that the DMP decomposition has mainly occurred in the solid matrix after sample deposition and not during deposition. The absorption at 1051 cm^{-1} appears, according to its relative intensity, to be associated with the OH-containing species and must belong to a CH_3 deformation and not a C–O stretching vibration, as will be shown below in the experiments with perdeuterated DMP.

Pyrolysis and Photolysis of CD_3OOCD_3. Figure 3 depicts the results of the thermal and photolytic decomposition of perdeuterated dimethyl peroxide. The mole ratios were in all cases 400 and the temperature of the internal window was kept in all experiments between 8 and 10°K. Trace I shows the spectrum of the CD_3OOCD_3 starting material in argon matrix. The very weak absorptions marked by b are due to window background and those marked by a diamond and an asterisk are due to traces of CO_2 and CD_2O, respectively. Trace K demonstates the spectral changes when the temperature of the inlet tube was increased from 25 to 210° during sample deposition. The principal decomposition products are CD_2O and CD_3OD. The bands assigned to CD_2O are marked by an asterisk. Their frequencies agree well with those reported[14] for gaseous CD_2O. The bands due to CD_3OD show again the pattern characteristic for mono-, di-, and polymeric species, as can be seen by comparison with the spectrum of a mixture of CD_3OD and CD_3OH in argon matrix (trace M). Trace L shows the spectrum of the deposit of trace I after exposure to uv irradiation at 8°K for 40 min using a water filter. By analogy with the DMP photolysis, CD_2O and CD_3OD were formed. Furthermore, the shifts of the OD and CO frequencies indicate that CD_3OD and CD_2O are located in the same matrix cage. Comparison of trace K (Figure 3) with trace C (Figure 1) shows that the absorption at 1051 cm^{-1} in C has shifted to 779 cm^{-1} in K and, hence, cannot be due to a C–O stretching vibration but must be ascribed to a CH_3 rocking mode. The relative intensity of the 779-cm^{-1} band in K has increased over that of the 1051-cm^{-1} band in C owing to its coincidence with the O–D in-plane deformation vibration of CD_3OD. This conclusion is further supported by comparison of traces K and L. The 779-cm^{-1} band in K has shifted to 813 cm^{-1} in L, as expected from the decreasing ν_{O-D} frequency from K to L. It is impossible to say whether a detectable amount of CO has formed in the CD_3OOCD_3 decomposition experiments, since the CD_3 stretching vibrations occur in the same range as the CO vibration and would mask any CO absorption band. Controlled-diffusion experiments were carried out for both the pyrolysis and photolysis products, but did not yield any conclusive information owing to line broadening.

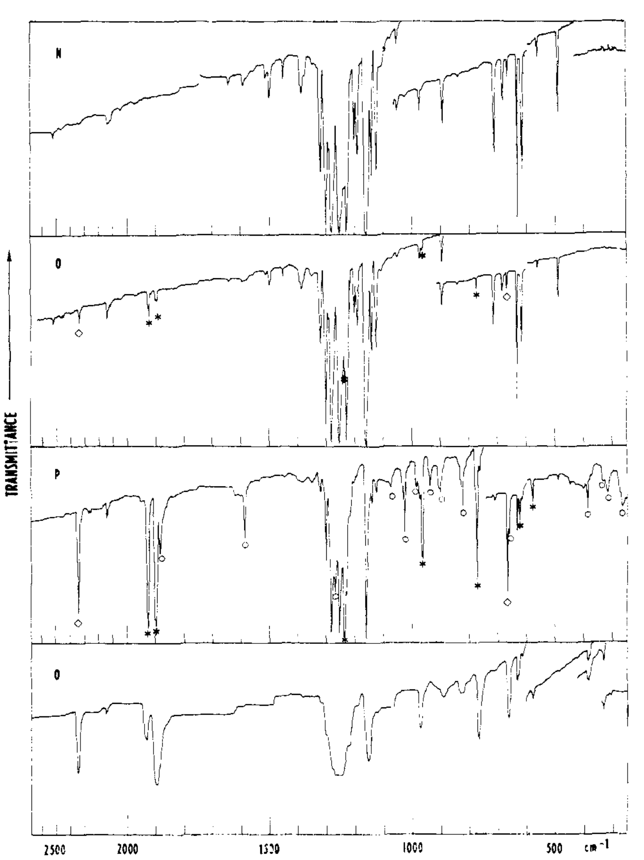

Figure 4. Pyrolysis of CF_3OOCF_3. For explanatory remarks, see Results section.

Pyrolysis and Photolysis of CF_3OOCF_3. Figure 4 shows the results obtained for the thermal and photolytic decomposition of CF_3OOCF_3. The mole ratio was in all cases 400 and the temperature of the internal window was kept between 8 and 10°K. Trace N depicts the spectrum of the CF_3OOCF_3 starting material in argon matrix and agrees well with that[15] previously reported. Exposing the deposit at 10°K for 40 min to water-filtered uv irradiation did not noticeably change its spectrum. Trace O was recorded after heating the inlet tube to 210° during sample deposition. The only new products formed are traces of CO_2 (marked by

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(14) H. Siebert, "Anwendungen der Schwingungspektroskopie in der Anorganischen Chemie," Springer-Verlag, West Berlin, 1966, p 55.

(15) J. R. Durig and D. W. Wertz, *J. Mol. Spectrosc.*, **25**, 467 (1968).

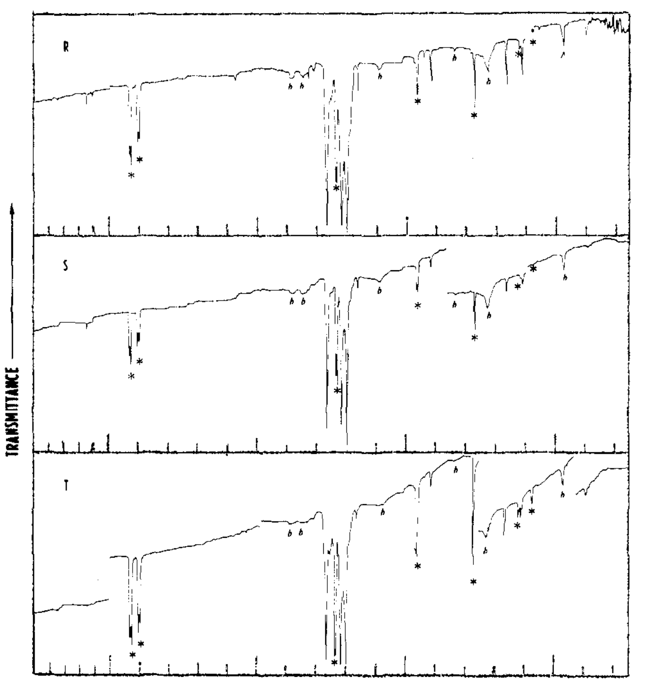

Figure 5. Photolysis and pyrolysis of CF_3OCl. For explanatory remarks, see Results section.

diamonds) and of COF_2 (marked by asterisks). Trace P shows the result of heating the inlet tube to 310° during sample deposition. The percentage of CO_2 and COF_2 has strongly increased. The frequencies and relative intensities observed for CO_2 and COF_2 in the argon matrix agree well with those reported for gaseous CO_2[16] and COF_2.[17] The splitting of ν_1 (A_1) of COF_2 into two band pairs in the matrix spectrum can be explained by Fermi resonance with $2\nu_2$ (A_1). In addition to the bands attributed to CF_3OOCF_3, COF_2, and CO_2 there are new absorptions (marked by a circle) at 1897, 1592, 1271, 1076, 1025, 986, 936, 899, 824, 659, 389, 336, 319, and 268 cm^{-1}. Trace Q shows the results of briefly warming the deposit of trace P to 42°K. It seems that after this controlled-diffusion experiment the bands at 1897, 899, 824, 389, and 336 cm^{-1} are still present, whereas the bands at 1592, 1025, 986, 936, 319, and 268 cm^{-1} have disappeared. Whether the bands at 1271, 1076, and 659 cm^{-1} have disappeared or not is difficult to say.

Pyrolysis and Photolysis of CF_3OCl. Figure 5 depicts the results obtained for the thermal and photolytic decomposition of CF_3OCl. In all cases the mole ratio was 400 and the temperature of the internal window was kept between 10 and 13°K. Trace R was recorded for the CF_3OCl starting material in argon matrix. It contains some COF_2 (bands marked by an asterisk), which always formed upon storage of CF_3OCl in the metal line prior to sample deposition. Several weak bands (marked by b) are due to cell-window background. The remaining bands are ascribed to CF_3OCl and agree well with those observed[8] for gaseous CF_3OCl. The two unassigned bands at 1095 and 730 cm^{-1} previously reported[8] for gaseous CF_3OCl were absent in the gas and matrix spectra of our CF_3OCl sample and are due to traces of CF_3CF_2OCl.[8] Exposure of the deposit of trace R at 13°K to water-filtered uv irradiation for 40 min did not result in any detectable changes. Trace S shows the results of water-filtered uv irradiation during sample deposition. Comparison of traces R and S demonstrates that the relative percentage of COF_2 has increased for S. No additional changes can be detected. Trace T was recorded when CF_3OCl was pyrolyzed at 190°. Again COF_2 is the only product detectable by infrared spectroscopy.

Discussion

Pyrolysis and Photolysis of CH_3OOCH_3 and CD_3OOCD_3. The only decomposition products detected in the thermal and uv decomposition of CH_3OOCH_3 and CD_3OOCD_3 were formaldehyde and methanol. No evidence for the formation of appreciable amounts of methoxyl radicals was obtained. Even if one assumes that the vibrational spectrum of the methoxyl radical might closely resemble that of dimethyl peroxide, the number of fundamental vibrations should decrease from 24 in CH_3OOCH_3 to 6 in $CH_3O\cdot$, thus causing a noticeable change in the relative intensity of some of the bands. However, this was not the case. The first step in the decomposition of DMP should be the previously suggested[1,3] split of the O–O bond according to

$$CH_3OOCH_3 \longrightarrow 2CH_3O\cdot \qquad (1)$$

The observation of CH_3OH and CH_2O as the only detectable products, however, suggests that the methoxyl radicals are highly reactive and cannot be isolated under the given reaction conditions.

The formation of CH_3OH and CH_2O within the same matrix cage in the uv photolysis of CH_3OOCH_3 at 8°K is due to the fact that the fragments are too large to be able to diffuse out of the cage. The two methoxyl radicals could recombine to CH_3OOCH_3 or hydrogen transfer from one methoxyl radical to the other one could take place, thus producing CH_3OH and CH_2O. This hydrogen migration would be analogous to that suggested[18] by Milligan for the photolysis of CH_3N_3 at 4.2°K. Instead of the expected CH_3N radical, he observed only $CH_2{=}NH$ and suggested that its formation might be due to rearrangement of a "hot" methylimino radical. Since the hypothetical CH_3N and CH_3O radicals should be quite similar in nature, similar behavior would not be surprising. Instead of an intermolecular hydrogen transfer one might also envisage an intramolecular transfer of the kind $CH_3O\cdot \rightarrow \cdot CH_2OH$, followed by the combination of the two CH_2OH radicals to form ethylene glycol. The existence of CH_2OH radicals is well established and ethylene glycol has, for example, been formed in the radiolysis of CH_3OH.[19] However, no evidence for the formation of $HOCH_2$–CH_2OH was observed in the photolysis of CH_3OOCH_3.

For the thermal decomposition of DMP there is a marked difference between the products observed in our experiments and those observed[1] by Hanst and Calvert. The latter authors could not detect any CH_2O in the products which approached the following stoichiometry

$$2CH_3OOCH_3 \longrightarrow 3CH_3OH + CO \qquad (2)$$

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(16) E. K. Plyler, L. R. Blaine, and E. D. Tidwell, *J. Res. Nat. Bur. Stand., Sect. A*, **55**, 183 (1955).

(17) J. Overend and J. C. Evans, *Trans. Faraday Soc.*, **55**, 1817 (1959).

(18) D. E. Milligan, *J. Chem. Phys.*, **35**, 1491 (1961).

(19) L. A. Tikhomirov, V. S. Palev'ev, and N. Ya. Buben, *Khim. Vys. Energ.*, **2**, 284 (1968).

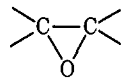
Since Hanst and Calvert carried out their experiments at much higher DMP pressures (3–30 Torr) and used much longer contact times (15–130 min), the disappearance of CH_2O and formation of CO must be due to secondary reactions. This is also confirmed by the gas-phase uv-photolysis study[3] of Toth and Johnston, who found that the observed amount of CH_2O decreased with increasing reaction time. One might argue that the failure to observe CO in our experiments is due to the fact that CO is a weak infrared absorber. However, the formation of CO from CH_2O should proceed through an intermediate HCO radical which has previously been matrix isolated[11,12,20] and is a reasonably strong infrared absorber. Since there is no evidence for an absorption in the 1860-cm^{-1} region of our spectra the presence of HCO and hence also CO is unlikely.

Olgilvie found[12] in a reinvestigation of the matrix spectra of the HCO radical a new band at 1100 cm^{-1} which he tentatively ascribed to the methoxyl radical. However, the observed behavior[12] of the new species upon controlled warm-up disagrees with his assignment. In the present investigation no new bands were observed at 1100 cm^{-1}.

The results obtained for the decomposition of CD_3OOCD_3 agree well with those obtained for CH_3OOCH_3. Furthermore, the observed isotopic shifts help to generally clarify the assignments. A detailed discussion of the infrared and Raman spectrum of CH_3OOCH_3 and CD_3OOCD_3 will be reported[21] in a separate paper. The matrix spectra of CH_3OH and of the CD_3OD–CD_3OH mixture indicate that the assignments[22] for the methyl rocking vibration in methanol might need revision.[23]

Pyrolysis and Photolysis of CF_3OOCF_3. Perfluorodimethyl peroxide is likely to produce upon decomposition free radicals more stable than those from CH_3OOCH_3. This expectation is based on bond-energy considerations.[4] On the other hand, the thermal and shock stability of CF_3OOCF_3 indicates a considerably stronger O–O bond, as is also expected from comparison with the analogous couple, HOOH and FOOF.[24,25] Consequently, a higher activation energy will be required to decompose CF_3OOCF_3, and it is difficult to predict which bond, *i.e.*, C–O or O–O, will rupture first. Thus, Vanderkooi and coworkers were able to show[26] by esr spectroscopy that photolysis of a solution of CF_3OOCF_3 at −196° produced the $CF_3OO\cdot$ and not the expected $CF_3O\cdot$ radical.

Our attempts to photolytically decompose CF_3OOCF_3 at 10°K in an argon matrix were unsuccessful. The increase in activation energy required for the decomposition of CF_3OOCF_3 was also demonstrated in the pyrolysis experiments. An inlet tube temperature of about 300° was necessary in order to observe an appreciable amount of decomposition products. The main decomposition products were COF_2 and CO_2. This is in good agreement with the observation by Porter and Cady[27] that CF_3OOCF_3 starts to decompose at 325° to form COF_2 and several other unidentified products. No evidence for the formation of CF_3OF was obtained. The formation of CF_3OF might have been expected, since CF_3OF and COF_2 are known[27] to combine to CF_3OOCF_3 and since COF_2 had been observed in our study as a major decomposition product. The additional unassigned bands must be due to at least two different species, since one set of bands disappears upon controlled diffusion at 42°K. The thermally less stable compound shows prominent absorptions at 1592 and 1025 cm^{-1}. The 1592-cm^{-1} band is difficult to assign since it is too low for a carbonyl- or a fluorine-substituted C=C group and it is too high for a C—F or C—O single-bond vibration. The most plausible explanation is that it belongs to a highly strained three-membered ring, such as



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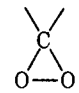
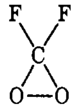


An unstable intermediate containing the latter ring system could be



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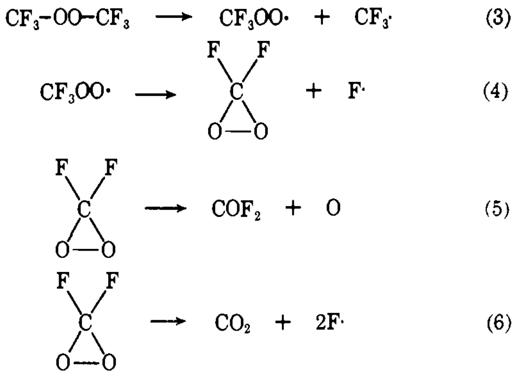
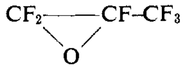
which might be formed according to the following simplified reaction scheme



The assumption of **1** as an intermediate in the decomposition of CF_3OOCF_3 could also account for the formation of both major products, COF_2 and CO_2, and for the absence of CF_3OF. The COC ring in



has its characteristic infrared absorption[28] at about 1540 cm^{-1} and, hence, a frequency of 1592 cm^{-1} does not seem unreasonable for a three-membered ring. The new band at 1025 cm^{-1} is within the range expected for C–F stretching vibrations. A positive identification of the new species is not possible due to the com-

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(20) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **41**, 3032 (1964).

(21) K. O. Christe, *Spectrochim. Acta, Part A*, in press.

(22) M. Falk and E. Whalley, *J. Chem. Phys.*, **34**, 1554 (1961).

(23) See also A. J. Barnes and H. E. Hallam, *Quart. Rev., Chem. Soc.*, **23**, 392 (1969).

(24) R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.*, **88**, 2394 (1966).

(25) S. J. Turner and R. D. Harcourt, *Chem. Commun.*, 4 (1967).

(26) N. Vanderkooi, Jr., and W. B. Fox, *J. Chem. Phys.*, **47**, 3634 (1967).

(27) R. S. Porter and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 5628 (1957).

(28) R. D. Wilson, unpublished results.

plexity of the system and is beyond the scope of this study.

Pyrolysis and Photolysis of CF_3OCl. Since CF_3OF appears to be a good precursor for generating $CF_3O\cdot$ radicals,[29] CF_3OCl, having an even weaker O–halogen bond, was studied. The photolytic gas-phase decomposition of CF_3OCl producing CF_3OOCF_3 and Cl_2 in high yields[8] indicates the formation of an intermediate $CF_3O\cdot$ radical. However, photolysis of CF_3OCl at 13°K in Ar matrix was ineffective, and photolysis in the gas phase during sample deposition and pyrolysis produced COF_2 as the only new product. The lack of evidence for a $CF_3O\cdot$ radical indicates either that the $CF_3O\cdot$ radical is very short lived, decomposing rapidly to COF_2, or that CF_3OCl decomposes under the given conditions in a reversal of its formation reaction

$$CF_3OCl \longrightarrow COF_2 + ClF \qquad (7)$$

The presence of ClF as by-product could not be established; however, ClF is known to be an extremely weak infrared absorber, and, hence, may have escaped detection.

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[29] W. A. Shepard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, p 220.

Chemical Ionization Mass Spectrometry of Borazine

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Abstract: Chemical ionization mass spectra of borazine in methane, ethane, *n*-butane, and ammonia have been obtained. Protonation of borazine to form $H_3B_3N_3H_4^+$ and fragmentation by loss of H to form $H_2B_3N_3H_3^+$ are the major processes observed when methane is used as the source of reactant ions. Protonation reactions become relatively more important than fragmentation in the borazine–ethane system. The mass spectrum of borazine in *n*-butane consists almost exclusively of the ion species $H_3B_3N_3H_4^+$. A lower limit of 7.7 eV is set for the proton affinity of borazine. Borazine undergoes addition reactions with $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ to form complexes assumed to be protonated *B*-alkylborazine ions. A complex species, $(NH_3)H_2B_3N_3H_3^+$, is observed in the borazine–ammonia system.

Borazine ($H_3B_3N_3H_3$) is frequently referred to as "inorganic benzene"[1] because of its structural similarity to benzene. However, the chemical behavior of the two compounds differs in many respects. One of the unique features of borazine, owing to the heterocyclic nature of the B–N ring, is its tendency to form adducts readily by addition of simple acids or bases. As a new approach to the study of this feature of borazine chemistry, we have employed the procedure referred to by Field[2] as chemical ionization mass spectrometry to investigate gas-phase ion–molecule reactions of borazine. The sources of ion reactants include CH_4, C_2H_6, n-C_4H_{10}, and NH_3.

Experimental Section

The mass spectrometer used in these experiments was a 10-in., 60° direction-focusing instrument. The chemical ionization source was constructed by modifying the ion box associated with a Nier-type source used for electron bombardment work. The ion box was sealed except for a 0.002 × 0.4 in. exit slit and a tapered opening on the side to accept a $^5/_{20}$ male joint from a glass delivery tube. This tube was joined by a small piece of flexible Teflon tubing to another glass tube that passed out the vacuum wall through a Swagelok-type fitting to the gas source. The analyzer and source compartments of the mass spectrometer were separated by a 0.007 × 0.4 in. slit, and each section was pumped with a 4-in. diffusion pump using Dow Corning 705 silicone pump fluid. Our ion source differs in several respects from those of other workers, and some differences in operating conditions should also be noted.

In initial experiments, iridium filaments were used for the source of electrons for ionization, but these were destroyed at high source pressures, apparently due to the presence of boron compounds. Tungsten filaments were found to be dependable up to source pressures of 3 mm and, for short periods, at source pressures as high as 4.5 mm. For most of the experimental observations the electron energy was maintained at 80 V. It was noted in test runs with methane that the CH_5^+/CH_4^+ ratio decreased for a constant source pressure as the electron energy was reduced to 50 V. The two drawing-out plates located above the source slit could be maintained at potentials of between 0 and −280 and 0 and −450, respectively. Variation in these potentials affected greatly the overall ion sensitivity but did not have a marked effect on the CH_5^+/CH_4^+ ratios. A small residual CH_4^+ signal was noted at source pressures as high as 2 mm. The ion accelerating voltage was maintained at 2800 V.

Gas mixtures were prepared by measuring the partial pressure of a sample of borazine in a 2-l. bulb with a silicone oil manometer and then adding a quantity of the reagent gas to bring the final pressure to a desired value from which the composition could be obtained. Gas flow to the ion source from the sample bulb was regulated through a Nupro fine metering valve with vernier handle. The gas pressure in the ion-source delivery tube was measured with a McLeod gauge. In a different series of experiments, a small quantity of borazine was injected through a metering valve into the hydrocarbon gas stream in front of the source entrance. With this procedure the hydrocarbon gas pressure could be maintained at a constant level while the effect of chemical ionization could be noted by comparing relative ion intensities before and after the addition of borazine. Borazine was prepared from *B*-trichloroborazine by the procedure of Hohnstedt and Haworth.[3] Methane, ethane, butane,

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[1] A. Stock in "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 97.

[2] M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).